

AD-A051 308

CALIFORNIA UNIV BERKELEY DEPT OF CHEMISTRY
CROSSED MOLECULAR BEAM STUDY OF THE REACTIONS OF OXYGEN AND FLU--ETC(U)
MAR 78 Y T LEE

F/G 20/8

N00014-75-C-0671

UNCLASSIFIED

UC-75-C-0671-78

NL

| IOF |
AD
A051308



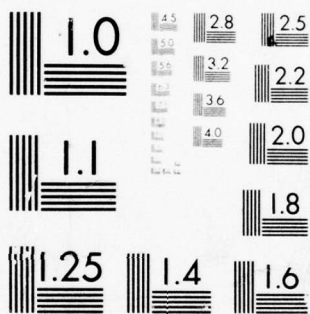
END

DATE

FILMED

4-78

DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A 051308

UUC FILE COPY

Security Classification

DOCUMENT CONTROL DATA - R & D

Enclosure 3

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

University of California
Berkeley, California 947202a. REPORT SECURITY CLASSIFICATION
No Restriction

2b. GROUP

3. REPORT TITLE

Crossed Molecular Beam Study of the Reactions of Oxygen and Fluorine Atoms

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Annual Report. Jan 77-Feb 78

5. AUTHOR(S) (Last name, middle initial, first name)

Yuan T./Lee

6. REPORT DATE

March 1, 1978

7a. TOTAL NO. OF PAGES

32

7b. NO. OF REFS

17

8a. CONTRACT OR GRANT NO.

N00014-75-C-0671

9a. ORIGINATOR'S REPORT NUMBER(S)

UC-75-C-0671-78

8b. PROJECT NO.

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

ONR - Power Program

13. ABSTRACT

With a high intensity monoenergetic $O(^3P)$ beam source developed during the previous contract period, we have succeeded in carrying out several reactions of oxygen atoms by crossed molecular beams experiments.

In the first two sections, the measurements of $O + ICl$, $O + C_2H_5I$ and CF_3I will be summarized. In addition to obtaining the detailed information on reaction dynamics, there are two very important results worth noting here. 1) The IO bond strength was found to be 53 ± 1 kcal/mole, rather than 44 ± 4 kcal/mole listed in NBS tabulation. 2) In $O + C_2H_5I \rightarrow C_2H_5 + IO$, the translational energy distributions of IO measured is higher than what was expected from statistical theory. It is much closer to the distribution if one neglects all vibrational degrees of freedom involving hydrogen atoms. On the other hand, in the reaction of $O + CF_3I \rightarrow CF_3 + IO$, the translational energy distributions agree exactly with statistical theory. These results imply that in the average reaction lifetime of $\sim 10^{-12}$ for these reactions, the intramolecular relaxation is quite effective among low vibrational frequencies but the internal energy is not effectively shared by high frequency vibrational modes.

In the third section, we will summarize our further studies on the intramolecular energy transfers in chemically activated radicals. A series of experiments including $Cl + 1$ -bromopropene, $Cl + 2$ -bromopropene and $Cl + 3$ -bromopropene were carried out. Here, we have demonstrated again, from the measurement of the translational energy distribution, that the high frequency vibrations which involve H-atoms do not share activation energy effectively before decomposition.

DD FORM 1473 (PAGE 1)
1 NOV 65

S/N 0101-807-6801

Security Classification

Molecular Beams Chemistry

LINK C

WT

DD FORM 1473 (BACK)
(PAGE 2)

Annual Summary Report Prepared for

Power Program
Office of Naval Research
Arlington, Virginia

By

Yuan T. Lee
Professor of Chemistry
Department of Chemistry
University of California
Berkeley, California 94720
Soc. Sec. No. 555-68-7196

CROSSED MOLECULAR BEAM STUDY OF THE
REACTIONS OF OXYGEN AND FLUORINE ATOMS

Reporting Period: January 1977 to February 1978

Contract No: N00014-75-C-0671

Reproduction in whole or in part is permitted
for any purpose of the United States Government.
The research was sponsored by the Office of
Naval Research (N00014-75-C-0671).

I. Progress Report (January 1, 1977 to December 31, 1977)
Crossed Molecular Beam Study of the Reactions of Oxygen
Atoms and Fluorine Atoms

N00014-75-C-0671
Principal Investigator:
Yuan T. Lee

Introduction

With a high intensity monoenergetic $O(^3P)$ beam source developed during the previous contract period, we have succeeded in carrying out several reactions of oxygen atoms by crossed molecular beams experiments.

In the first two sections, the reactions of $O + ICl$, $O + C_2H_5I$ and CF_3I will be summarized. In addition to obtaining the detailed information on reaction dynamics, there are two very important results worth noting here. 1) The IO bond strength was found to be 53 ± 1 kcal/mole, rather than 44 ± 4 kcal/mole listed in NBS tabulation. 2) In $O + C_2H_5I \rightarrow C_2H_5 + IO$, the translational energy distributions of IO measured is higher than what was expected from statistical theory. It is much closer to the distribution if one neglects all vibrational degrees of freedom involving hydrogen atoms. On the other hand, in the reaction of $O + CF_3I \rightarrow CF_3 + IO$, the translational energy distributions agree exactly with statistical theory. These results imply that in the average reaction lifetime of $\sim 10^{-12}$ for these reactions, the intramolecular relaxation is quite effective among low vibrational frequencies but the internal energy is not effectively shared by high frequency vibrational modes.

1. Atomic Oxygen Source Development and a Study of the $O + ICl \rightarrow IO + Cl$ Reaction

Steven J. Sibener and Richard J. Buss

The long term stability and reproducibility of our high pressure radio frequency discharge beam source for the production of ground state oxygen atoms has been improved to the point where reactive crossed beam scattering experiments have been successfully carried out. Product angular distributions and time-of-flight velocity distributions have been obtained for reactions with three iodine containing compounds: ICl , C_2H_5I , and CF_3I . When a full analysis of all three systems is completed, we hope to refine the IO bond strength value proposed by Grice,¹ $D_0(IO) = 53 \pm 3$ kcal/mole. The previous spectroscopic value was $D_0(IO) = 42 \pm 5$ kcal/mole. Our preliminary results fall within Grice's error limits. The reactants in the $O + ICl$ reaction approach on a triplet potential energy surface. The possibility that a surface crossing might occur to a singlet surface, yielding $ClO + I$ as the reaction products, was also investigated. However, no ClO product was detected. All three experiments were carried out at a collision energy of approximately 3.3 kcal/mole. The energetics for the reactions studied are:

	ΔD_0 (kcal/mole)	
$O + ICl \longrightarrow IO + Cl$	3.4	(1)
$O + C_2H_5I \longrightarrow IO + C_2H_5$	0.0	(2)
$O + CF_3I \longrightarrow IO + CF_3$	-0.2	(3)
$O + CH_3I \nrightarrow IO + CH_3$	-3.3	(4)

Reaction (4) was also attempted but no IO product was detected,

In this report the analysis of the energetics and dynamics of the $O + ICl \rightarrow IO + Cl$ reaction will be discussed. The reaction is found to proceed via a long-lived collision complex whose IO product translational energy distribution can be described by RRKM-AM statistical theory (within the current uncertainties of the reaction energetics). The ICl was seeded in Argon to a translational velocity of 4.95×10^4 cm/sec and a Mach number of 7. The oxygen atoms were produced in our radio frequency discharge beam source with a peak translational velocity of 1.29×10^5 cm/sec and a Mach number of 4. Table 1 lists typical dissociation characteristics of the discharge source for two different nozzles. Molecular dissociation is always found to be greater than 80° and to depend weakly on RF power and nozzle pressure. The gas mixture used in these experiments was 95% Argon/5% O_2 .

Figure 1 shows the lab angular distribution and the most probable Newton diagram for the $O + ICl$ reaction. Significant lab intensity appears on both sides of the center-of-mass angle which is approximately 15° from the halogen beam direction. Cross-correlation time-of-flight (TOF) spectra taken at eight lab angles were combined with this angular distribution to give a center-of-mass contour map which is shown in Fig. 2. Both the forward (with respect to the oxygen beam direction) and backward scattered peaks are observed to peak along the relative velocity vector indicating the importance of angular momentum considerations for this reaction. The symmetry of the map is indicative of a long-lived collision complex. The forward peak has a much higher information content

than the backward peak since it is composed of six angles at which TOF spectra were taken in a low noise environment (far from the halogen beam). Hence further discussions in this report on the energetics of this reaction will be based exclusively on information from the forward scattered IO product peak.

Figure 3 compares the calculated best-fit flux distributions with the experimentally determined flux distributions for all eight angles at which TOF spectra were taken. These best fit distributions were deconvoluted and used in the construction of the canonical contour map described earlier. For the reaction under study the anisotropy ratio for the center-of-mass angular distribution, $\frac{I(\theta = 0^\circ)}{I(\theta = 90^\circ)}$, was found to be approximately 2.5. The contour map and anisotropy ratio obtained for our reaction at a collision energy of 3.3 kcal/mole are similar in form to Herschbach's³ O + Br₂ and Grice's⁴ O + I₂, ICl results, which were obtained with effusive atomic oxygen beams.

A product translational energy distribution was computed using information in the forward peak of the contour map. This is shown in Fig. 4. The RRKM-AM⁵ statistical predictions are also shown when E' = 6.7 kcal/mole and E' = 8.7 kcal/mole are assumed available for product translation (E' = collision energy + reaction exoergicity). The lower of these E' values assumes Grice's IO bond strength of 53 ± 3 kcal/mole. These two curves appear to define lower and upper bounds for the experimental P(E') distribution when the maximum exit centrifugal barrier of RRKM-AM theory, B_m['], is set at 0.75 kcal/mole. When final bounds are calculated for the CF₃I and C₂H₅I reactions a composite IO

bond strength will be determined. $D_0(I0) = 54 \pm 1.5$ kcal/mole appears consistent with the $P(E')$ distribution determined in this experiment.

In summary, our atomic oxygen reactive scattering program has begun successfully and will now proceed on to the study of combustion reactions with unsaturated hydrocarbons. We hope to determine the product channels and dynamics for these systems. Hopefully these studies will add significantly to our knowledge of the combustion process, since the products from these reactions are highly reactive free radicals which participate in subsequent chain branching reactions.

References

1. D. St. A. G. Radlein, J. C. Whitehead, and R. Grice, *Nature* 253, 37 (1975).
2. R. A. Durie and D. A. Ramsay, *Can. J. Phys.* 36, 45 (1958).
3. D. D. Parrish and D. R. Herschbach, *J. Am. Chem. Soc.* 95, 6133 (1973).
4. D. St. A. G. Radlein, J. C. Whitehead and R. Grice, *Mol. Physics* 29, 1813 (1975).
5. S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.* 12, 564 (1972).

Table 1. Molecular Oxygen Dissociation Characteristics

	Pressure (torr)	RF Power (watts)	Dissociation(percent)
Nozzle A	190	115	87.6
	190	120	88.1
	190	150	92.6
<hr/>			
Nozzle B	100	110	88.5
	150	110	85.2
	180	110	80.7

Figure Captions

Fig. 1. Angular distribution of reactively scattered IO product.

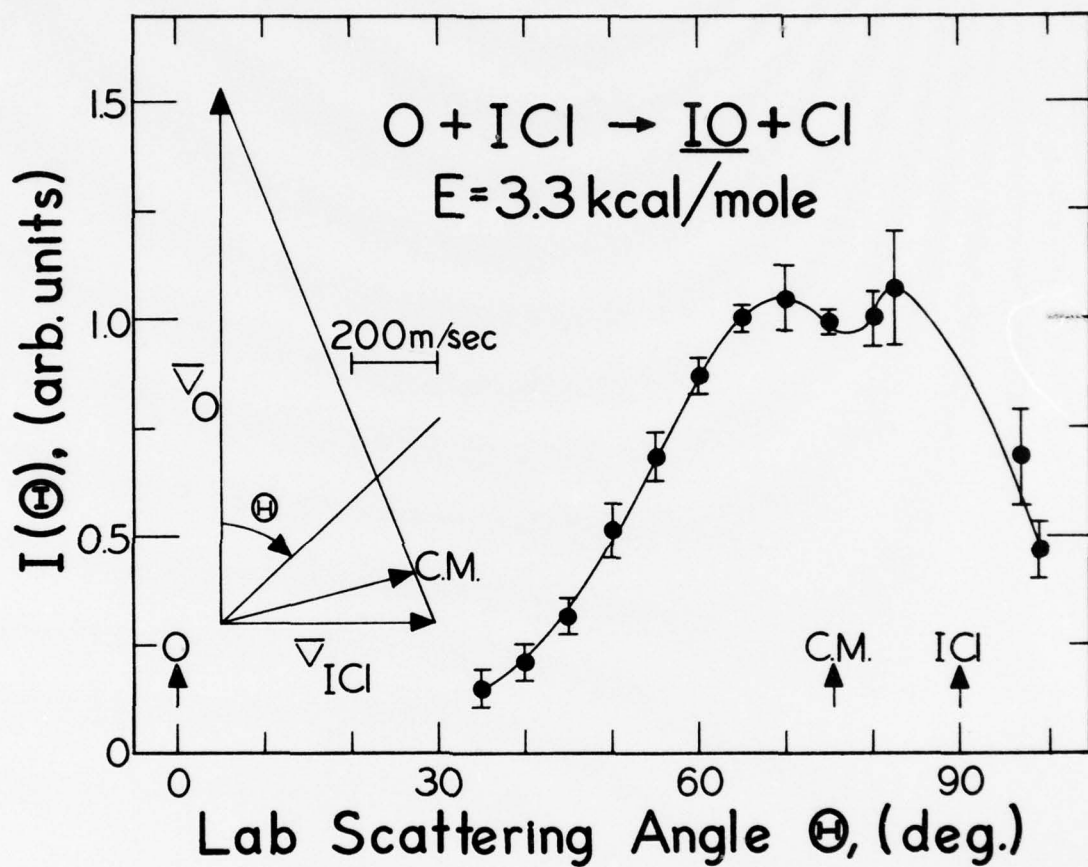
XBL-7712-10934

Fig. 2. Contour map of the IO product flux density in the center-of-mass coordinate system produced in the reaction $O + ICl$.

XBL-7712-10948

Fig. 3. Flux distributions for reactively scattering IO at eight laboratory angles. ● Experimental distributions obtained from cross-correlation TOF, ○ Calculated best-fit distributions. XBL-7712-10949

Fig. 4. Experimental product translational energy distribution (●) and calculated RRKM-AM distributions for the reaction $O + ICl$ at a collision energy of 3.3 kcal/mole. XBL-7712-10931



XBL 7712-10934

Fig. 1

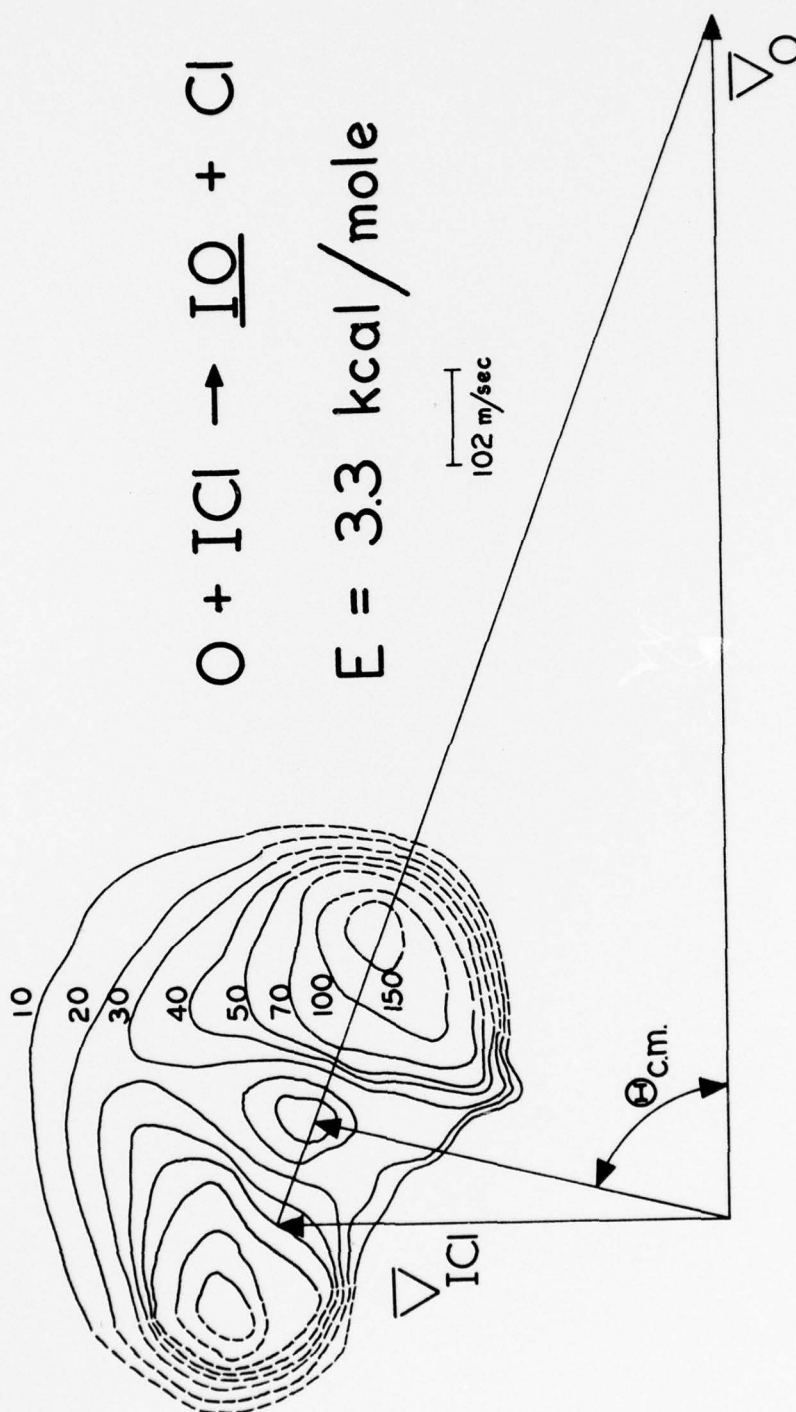


Fig. 2

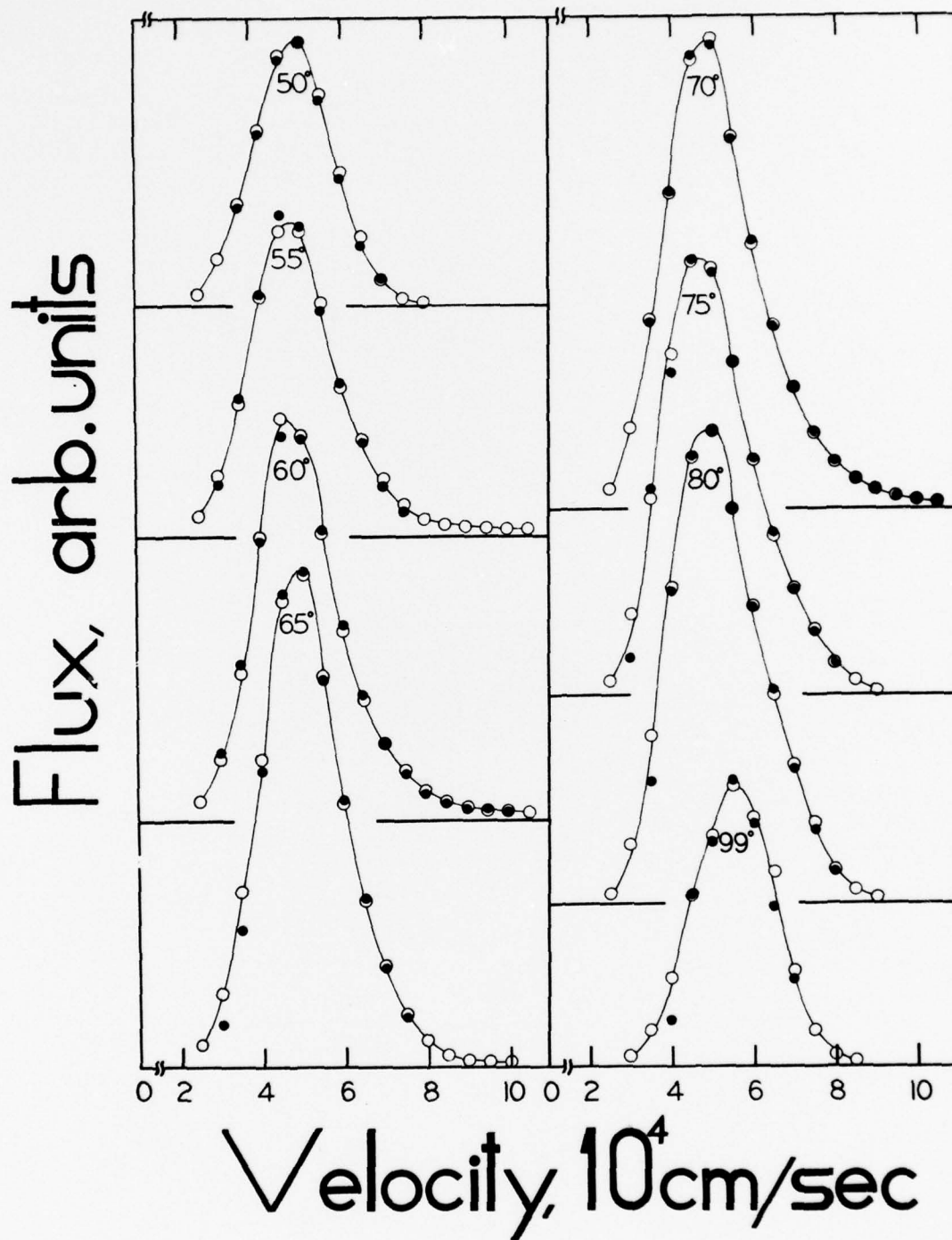
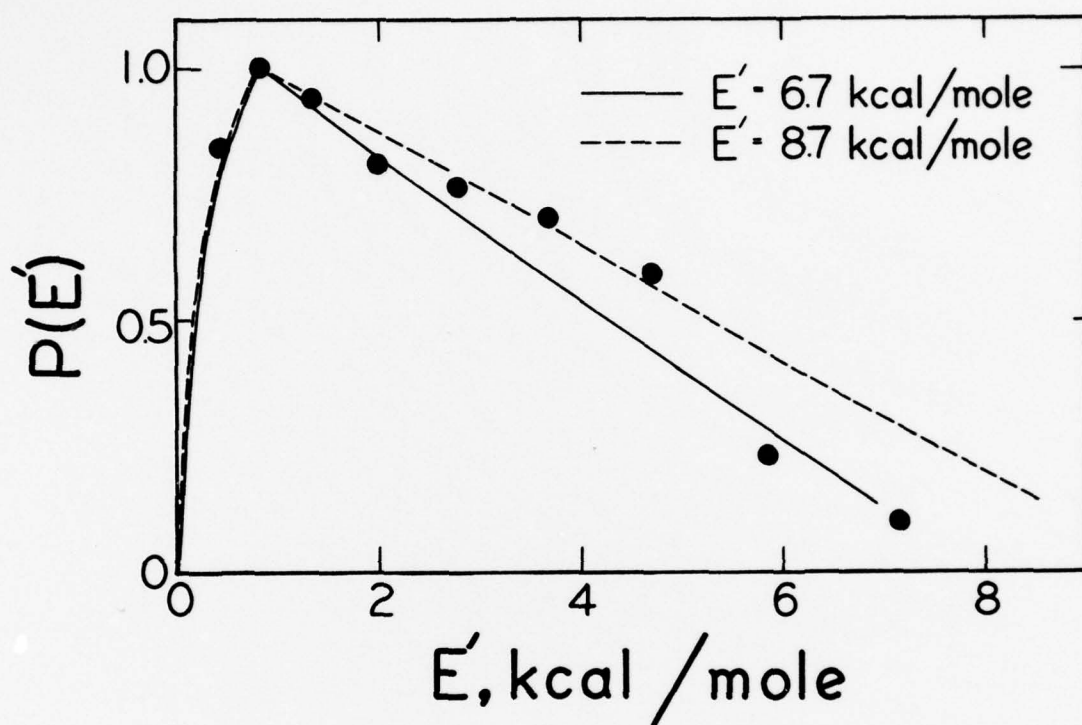


Fig. 3

XBL 7712-10949



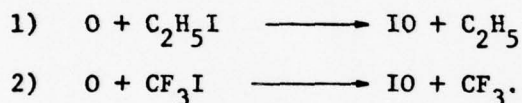
XBL 7712-10931

Fig. 4

2. Reactions of $O + C_2H_5I$ and $O + CF_3I$

R. J. Buss and S. J. Sibener

Recent studies of energy randomization in long lived complexes, have suggested that coupling between high and low frequency vibrations may be sufficiently weak as to prohibit the complete redistribution of energy. In the reactions of chlorine atoms with several bromo-olefins, both the vibrational and translational energy distributions exhibit nonstatistical behavior. Using the technique of crossed molecular beams, we have obtained product translational energy distributions for the iodine abstraction reactions:



While the IO product velocity distribution from 2 agrees well with statistical predictions, that for 1 deviates from the theoretical.

The oxygen atom beam was produced by RF discharge of a mixture of 5% O_2 in argon, at about 200 torr pressure. The peak velocity was measured to be 1.29×10^5 cm/sec and the mach number about 4. The ethyl iodide was run at vapor pressure from a 316 K oil bath, which produced a peak velocity of 6.5×10^4 cm/sec and mach number 10. With 250 torr CF_3I behind the .13 mm nozzle, the peak velocity was 3.4×10^4 cm/sec and the mach number, 6.4. The collision energy for both systems was about 3.3 kcal/mole.

The laboratory angular distributions are shown in Fig. 1, with error bars giving the 95% confidence limit for twelve scans. The IO product, mass 143, peaks at the center of mass, as expected from the

relative mass of the two fragments and the low exoergicity of the reaction. In both systems the information on the backward scattered product is insufficient to establish the presence of forward/backward symmetry. Velocity information obtained by cross-correlation time of flight of the product was used to produce the translational energy distributions shown in Figs. 2 and 3. It is significant that both distributions begin at zero energy, hence the products do not descend a repulsive barrier in the exit channel.

Shown in Fig. 2 are three RRKM calculations in which the exoergicity is varied. Angular momentum has been treated as described by Safron et al.¹ The agreement of the observed data is such that bounds can be set on the energetics of the reaction, $\Delta H = 0 \pm 1$ kcal/mole. Using published data for the ΔH_f of CF_3I and CF_3 ² we obtain an IO bond energy 53 ± 1 kcal/mole, in good agreement with that deduced from the reaction of $O + ICl$.³

The full RRKM calculation for the C_2H_5I reaction, with all vibrational modes assumed to be active and the IO bond energy 54 kcal/mole, is shown in Fig. 3. Substantially more translational energy is observed in the products than is predicted. Even when the exoergicity is assumed to be 4 kcal/mole (dashed curve in Fig. 3) the distribution is considerably narrower than that observed. The RRKM calculation in which hydrogen modes have been removed is in modest agreement with our data. It is of interest to note that for this latter molecule without hydrogen modes, the RRKM lifetime is .01 psec, which is far shorter than a rotational period. Indeed it

should be difficult for energy to randomize in the time scale of a single vibrational period.

These two reactions provide an interesting comparison. Although the energetics are quite similar, the reaction dynamics are altered by the internal frequency dispersion. It would appear that energy sharing by the hydrogen modes in C_2H_5I is prohibited by the large frequency difference.

References

1. S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, Chem. Phys. Lett. 12, 564 (1972).
2. H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. of Phys. and Chem. Ref. Data, Vol. 6, 1977, Supp. No. 1.
3. See report number 1 in this series.

Figure Captions

Fig. 1. Experimental laboratory angular distributions of IO product from the reaction of oxygen atoms with C_2H_5I and CF_3I .

XBL-7712-10935

Fig. 2. ● Observed product translational energy distribution of IO.

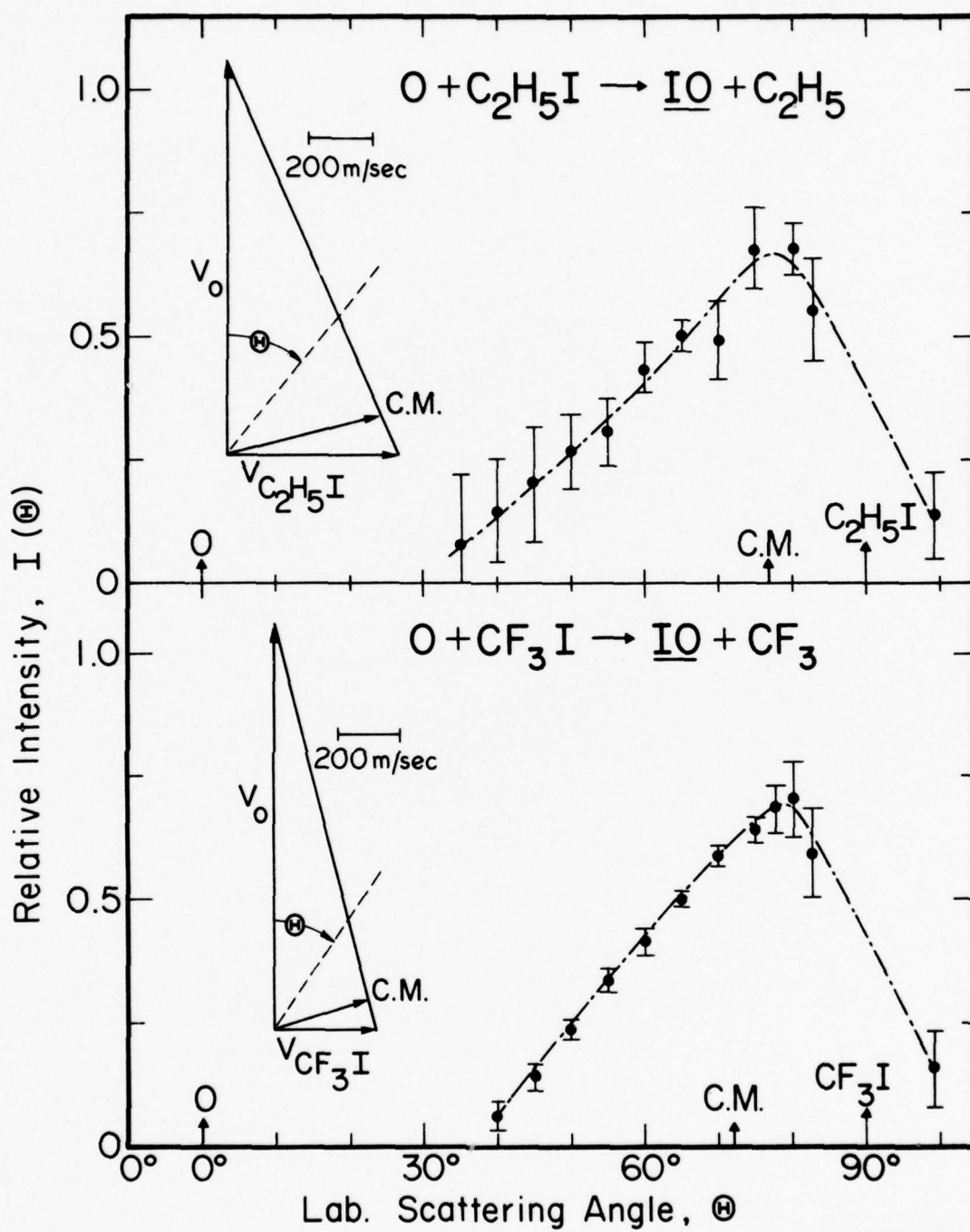
- - - - -	RRKM Calculation	$\Delta H = + 1.0$
— - —	RRKM Calculation	$\Delta H = 0.0$
— - - —	RRKM Calculation	$\Delta H = - 1.0$

XBL-7712-11072

Fig. 3. ● Observed product translation energy distribution of IO.

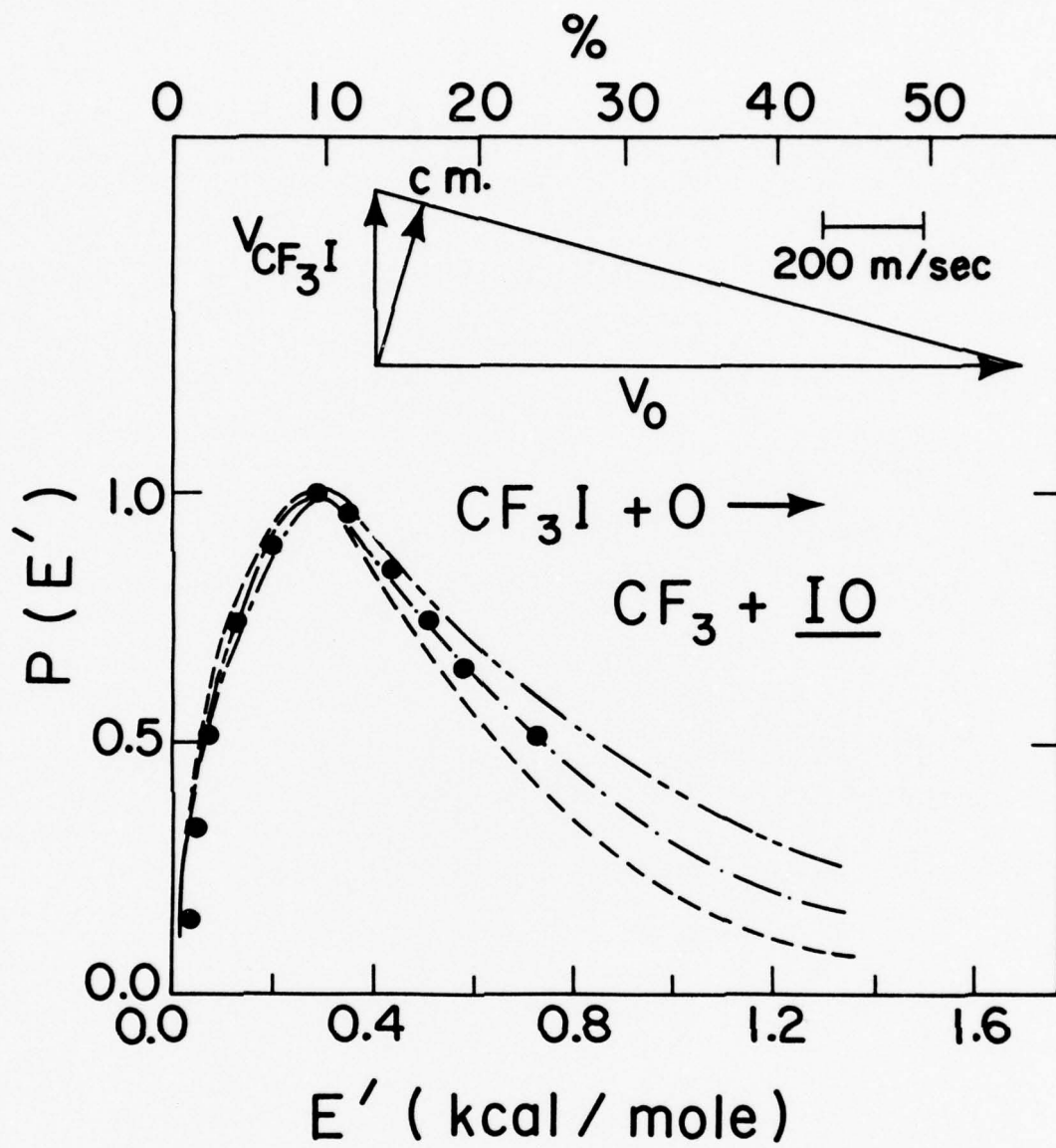
—————	RRKM Calculation	$\Delta H = - 1.0$	21 Active Vibrations
- - - - -	RRKM Calculation	$\Delta H = - 4.0$	21 Active Vibrations
— - —	RRKM Calculation	$\Delta H = - 4.0$	7 Active Vibrations

XBL- 7712-10965



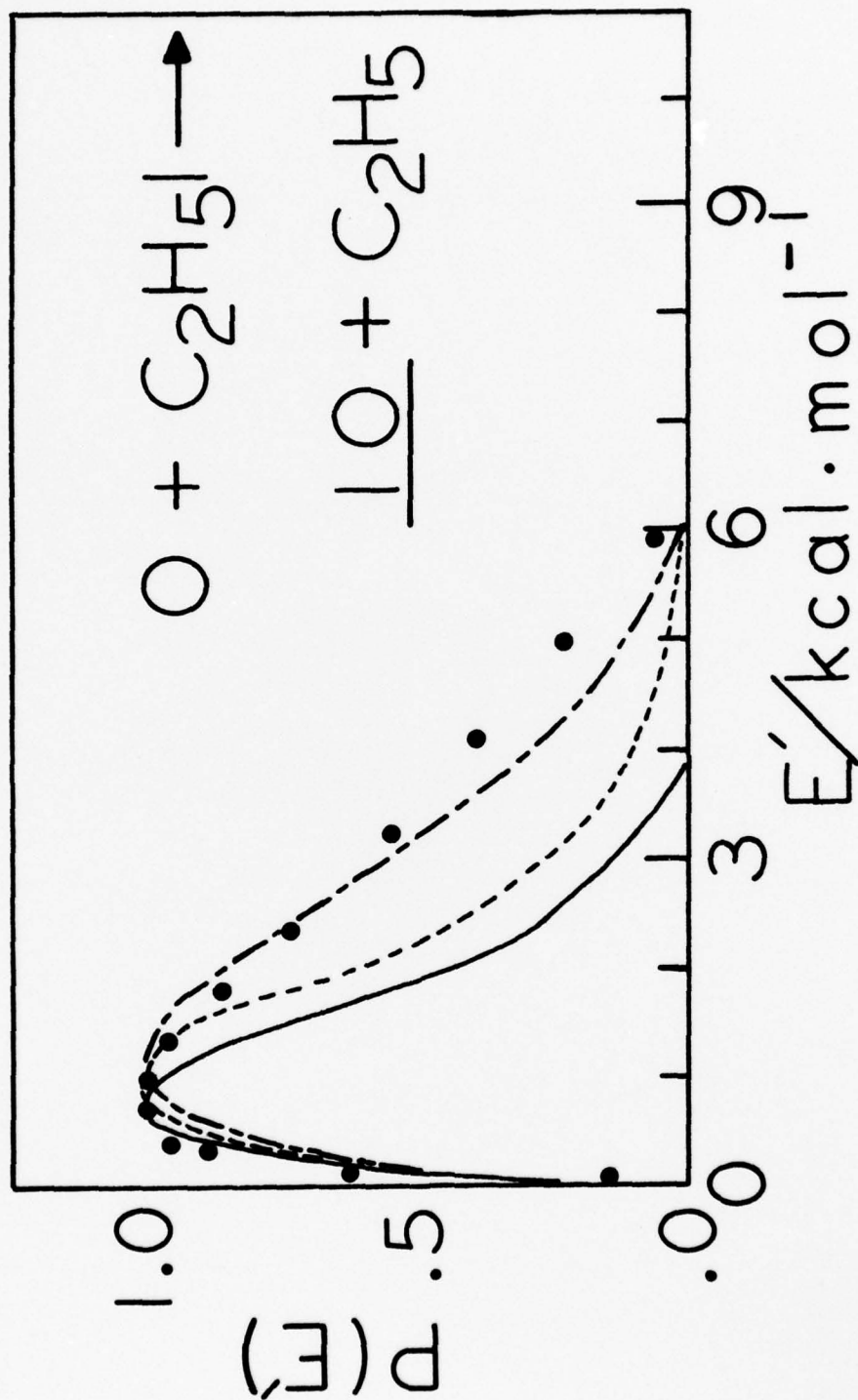
XBL 7712-10935

Fig. 1



XBL7712-11072

Fig. 2



XBL 7712-10965

Fig. 3

3. Substitution Reaction of Cl + Bromopropene

R. J. Buss and S. J. Sibener

In chemiluminescence studies of chlorine reacting with bromine-substituted olefins,¹ the product vibrational energy distribution has been shown to be nonstatistical. Calculations in which the energy of the long-lived complex is assumed to be randomly distributed over the internal degrees of freedom, predict more energy in the high frequency modes of the product than is actually observed. This suggests that coupling between the hydrogen modes and the skeletal modes of the complex is sufficiently weak that these high frequency ones do not share the energy released in the collisional activation. A recent study of the reaction $\text{Cl} + \text{C}_2\text{H}_3\text{Br} \rightarrow \text{Br} + \text{C}_2\text{H}_3\text{Cl}$ in crossed molecular beams² has shown that the product translational energy distribution does not agree with that predicted by the statistical theory. More energy appears as product translational than would be expected if all internal degrees of freedom are active in the complex. We have now used crossed molecular beams to look at the product angular and velocity distributions in the reactions of chlorine atoms with the three olefins; 1-bromopropene, 2-bromopropene and allyl bromide. The product translational energy of all three is found to be higher than the statistical theories predict.

The chlorine atoms were produced in a resistively heated graphite oven previously described.³ Time of flight analysis was used to determine the beam's peak velocity, 1.29×10^5 cm/sec and its mach number 9.0. The bromo-olefin beams were produced from the vapor pressure above the liquid in an ice bath with argon added to bring the total

pressure to 250 torr. The beams had mach numbers of 11.0. The beams collide at 90° giving a collision energy of 6.3 kcal/mole. The observed angular distributions are shown in Fig. 1, together with a typical Newton diagram. The error bars are 95% confidence limits on twelve, 100 second scans. The product mass 76.0 was detected as a weak contaminant of the olefin beam, and elastic scattering prevented observation of product scattered backward from the center of mass direction. Fractional distillation of the olefin failed to remove the contaminant. Velocity distributions were obtained at 5° intervals using the cross-correlation time of flight wheel with counting times of one to three hours at each angle. The product translational energy distributions are shown in Fig. 2.

The results of several statistical calculations are also shown in Fig. 2. Because the addition of bromine to olefins is known to proceed without an activation barrier, the analysis is not complicated by the existence of an exit channel barrier. The energetics of these three reactions (shown in Fig. 3) are quite similar. Using group contributions to the internal energy⁴ the exoergicity is estimated to be 12.5 kcal/mole and the complex is more stable than the reactants by 18.0 kcal/mole. The RRKM calculations with all internal degrees of freedom active, are shown as solid lines in Fig. 2. These distributions peak at lower energy and are far narrower than those observed. The dashed curves are the RRKM calculations in which the hydrogen modes have been removed. In the reactions of 1-bromo and 2-bromopropene, these calculated distributions agree quite well with the observed data. This suggests that the lifetime

of the complex is short enough that the energy initially released in formation of the carbon chlorine bond remains in the vibrations of the heavy atoms. This description is inadequate to explain the 3-bromopropene results.

The angular momentum in these reactions is treated according to the method proposed by Safron et al.⁵ The model assumes that for a loose complex the distribution of angular momentum will be linear in impact parameter up to a maximum value and zero thereafter. This approximation might be expected to be satisfactory for complexes in which the reactive site is coincident with the center of mass. In the reaction of chlorine with 3-bromopropene, the chlorine must attack the double bond which is considerably removed from the center of mass. Thus the angular momentum of the complexes might be considerably higher, on the average, than the linear approximation can allow. When the distribution of angular momentum in the complexes is changed to $P(b) = b^n$, with $n > 1$, the theory will predict more energy going to translation. In Fig. 2 the calculated distribution for $n = 3$ with all vibrations active gives a reasonably good fit to the data.

It is clear that the RRKM-AM calculation does not predict the correct product translational energy. This observation supports the results of the chemiluminescence experiments. As with the vinyl bromide reaction, there remains some doubt whether the angular momentum treatment is adequate for these reactions. We hope to answer this question by lowering the collision energy, thereby reducing the effect of angular momentum to a minimum.

References

1. J. F. Durana and J. D. McDonald, J. Chem. Phys. 64, 2518 (1976),
2. M. Coggiola, R. Buss and Y. T. Lee, unpublished results.
3. James Joseph Valentini, Reactive Scattering of Halogen Molecules, (Ph.D. Thesis), LBL-5746, November 1976.
4. S. W. Benson, Thermochemical Kinetics, John Wiley and Sons, Inc., New York, 1968.
5. S. A. Safron, N. D. Weinstein, D. R. Herschbach and J. C. Tully, Chem. Phys. Lett. 12, 564 (1972).

Figure Captions

Fig. 1. Experimental laboratory angular distributions of chloropropene produced in the reaction of $\text{Cl} + \text{C}_3\text{H}_5\text{Br}$ at collision energy 6.3 kcal/mole. XBL-7712-10933

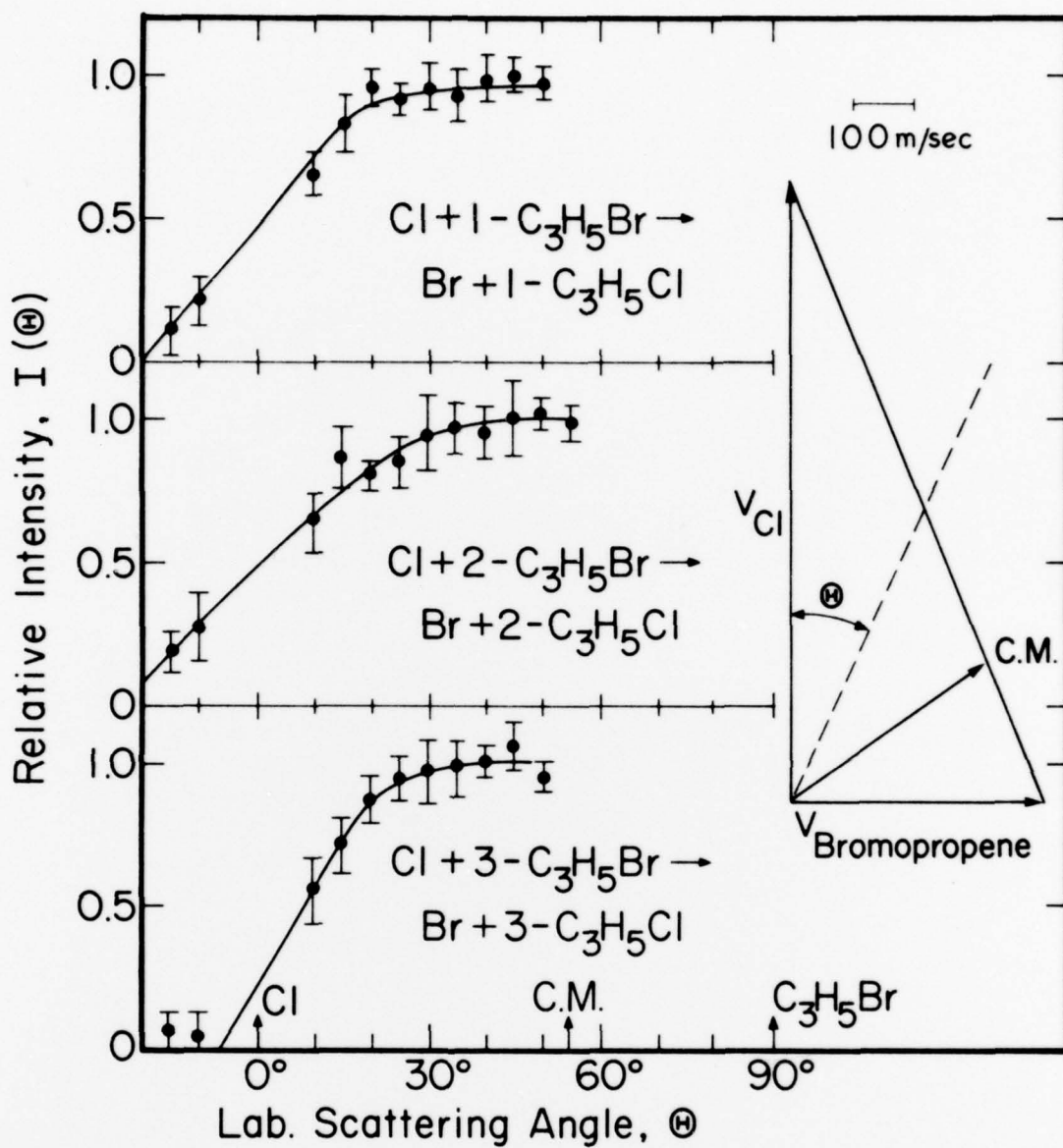
Fig. 2. ● Experimental product translational energy distribution .

-----	RRKM-AM Calculation	24 Active Vibrations
- - - - -	RRKM-AM Calculation	9 Active Vibrations
— - — - -	RRKM-AM with modified angular momentum treatment	24 Active Vibrations

XBL-7712-10906

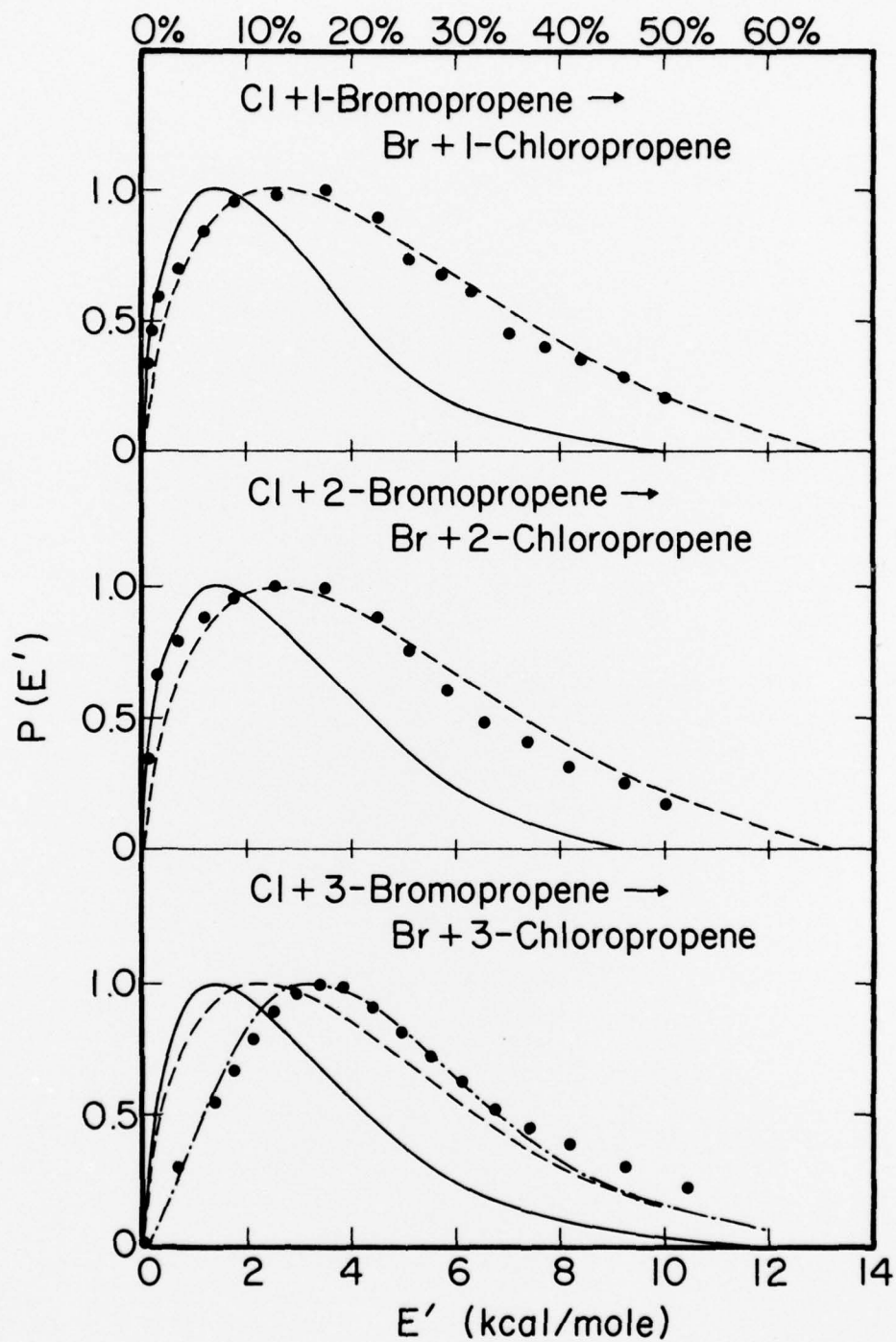
Fig. 3. Energetics of the reaction $\text{Cl} + \text{C}_3\text{H}_5\text{Br} \rightarrow \text{Br} + \text{C}_3\text{H}_5\text{Cl}$.

XBL-7712-10929



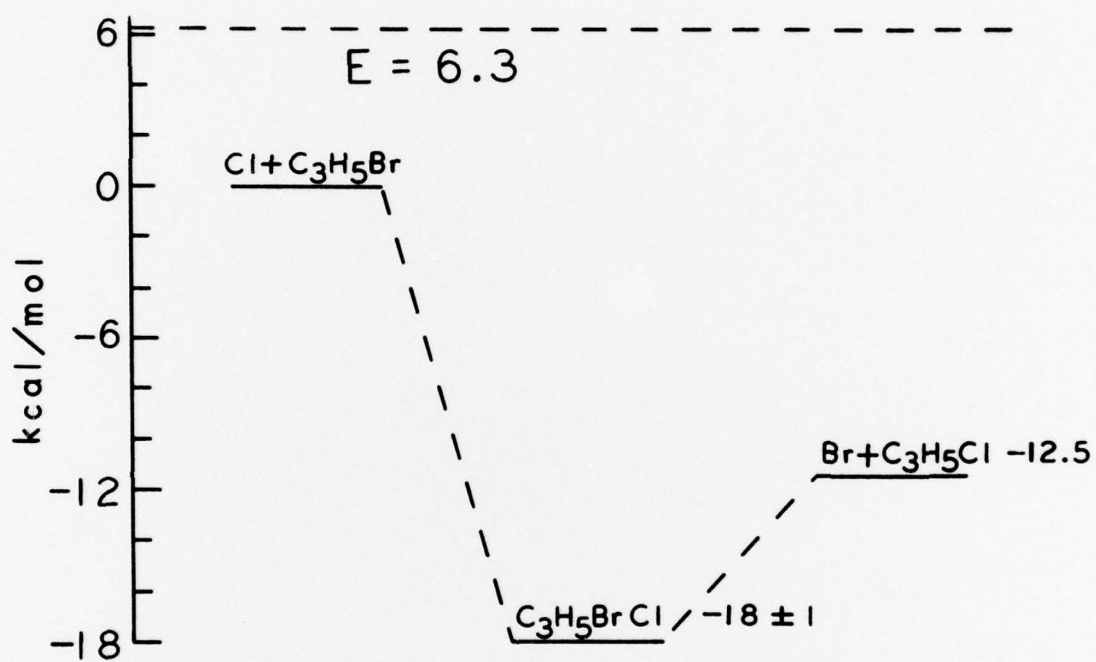
XBL 7712-10933

Fig. 1



XBL 7712-10906

Fig. 2



XBL 7712-10929

Fig. 3

II. Publication of ONR Supported Research (N00014-75-C-0671)

A. Paper published during 1977 supported by ONR contract:

1. The Binding Energy Between NO and NO⁺, C. Y. Ng, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, J. Chem. Phys. 66, 3985 (1977).

Abstract. The photoionization efficiency curve of the nitric oxide dimer (NO)₂ was obtained in the wavelength range from 1460 to 1210 Å (8.492-10.246 eV). The ionization potential of (NO)₂ was found to be 8.746 ± 0.015 eV. From this, the ionization potential of NO and the dissociation energy of (NO)₂ (0.069 ± 0.004 eV) obtained by Billingsley and Callear, the dissociation energy of NO(2Π, v" = 0)-NO⁺(1Σ⁺, v' = 0) is deduced to be 0.59 ± 0.02 eV. From the comparison of the structure of the photon yield curve of NO and (NO)₂ it is concluded that NO(2Π, v" = 0)-NO⁺(1Σ⁺, v') is bound when NO⁺(1Σ⁺) is in the v' = 0 or 1 vibrational state. This conclusion is in agreement with the dissociation energy of (NO)₂⁺ obtained.

2. Photoionization Studies of the Kr₂ and Ar₂ van der Waals Molecules, C. Y. Ng, D. J. Trevor, B. H. Mahan, and Y. T. Lee, J. Chem. Phys. 66, 446 (1977).

Abstract. The photoionization efficiency curves of the Kr₂ and Ar₂ van der Waals dimers were obtained with the molecular beam technique in the wavelength ranges 850-965 Å (12.848-14.586 eV) and 750-855 Å (14.501-16.531 eV), respectively. The ionization potential of Kr₂ was found to be 12.87 ± 0.015 eV (963.7 ± 1.2 Å), which agrees with the value obtained by Samson and Cairns. The ionization potential of Ar₂ was found to be 14.54 ± 0.02 eV (852.7 ± 1.2 Å). Using the known ground state dissociation energies of Kr₂ and Ar₂, the dissociation energy of Kr₂⁺, D₀(Kr₂⁺), is deduced to be 1.15 ± 0.02 eV and that for Ar₂⁺, D₀(Ar₂⁺), is 1.23 ± 0.02 eV. The photoion yield curves of Kr₂ and Ar₂ are compared with that of Xe₂. Prominent autoionization structure was observed to correspond to Rydberg molecular states which are derived from the combination of a normal and an excited atom in the 4p⁵nd configuration for Kr and 3p⁵ns (or 3p⁵nd) configuration for Ar.

3. Supersonic Atomic and Molecular Halogen Nozzle Beam Source, James J. Valentini, Michael J. Coggiola, and Yuan T. Lee, Rev. Sci. Instrum. 48, 58 (1977).

Abstract. A reliable, resistance heated nozzle beam source is described which is capable of producing high-intensity supersonic atomic and molecular beams of chlorine, bromine, and iodine. The use of a high-density graphite nozzle eliminates corrosion and allows

for operation up to 2300 K. The performance of this source is reported using seeded halogen gas mixtures which extend the accessible kinetic energy region to several eV.

4. Photoionization Studies of the Diatomic Heteronuclear Rare Gas Molecules XeKr, XeAr, and KrAr, C. Y. Ng, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, J. Chem. Phys. 66, 5737 (1977).

Abstract. The photoionization efficiency curves of the heteronuclear rare gas van der Waals molecules XeKr, XeAr, and KrAr were obtained with the molecular beam technique in the wavelength range from 790 to 1065 Å (11.64-15.69 eV). The ionization potentials were found to be 11.757 ± 0.017 eV for XeKr, 11.985 ± 0.017 eV for XeAr, and 13.425 ± 0.020 eV for KrAr. From the known dissociation energies of the ground state XeKr, XeAr, and KrAr van der Waals molecules as determined by low energy molecular beam elastic scattering experiments, the binding energies for the ground state of the heteronuclear rare gas molecular ions were deduced to be 0.37 ± 0.02 eV for XeKr⁺, 0.14 ± 0.02 eV for XeAr⁺, and 0.59 ± 0.02 eV for KrAr⁺. The photoion spectra of the heteronuclear rare gas dimers R₁R₂ exhibit prominent autoionization structure, which is found to correlate very well with the excited molecular Rydberg states R₁*R₂ and R₁R₂* formed by the interaction of a normal ground state rare gas atom R₁ (or R₂) and an excited atom R₂* (or R₁*), in the n'p⁵(²P_{1/2,3/2})ns (nd) configuration (where n' = 3 for Ar, n' = 4 for Kr, and n' = 5 for Xe). The excitation of XeKr, XeAr, and KrAr is found to obey the parity selection rule $\Delta l = \pm 1$, in agreement with previous experimental observations in the photoionization studies of Kr₂ and Ar₂. The Rydberg series 5p²(²P_{1/2})ns (nd) for Xe, and 4p⁵(²P_{1/2})ns (nd) for Kr, which is manifested as autoionization lines in the photoion spectra of the van der Waals rare gas dimers XeAr and XeKr, respectively, were red shifted with respect to the positions in the photoionization efficiency curves of Xe and Kr. This allows one to calculate the potential energy for the excited molecular Rydberg state at a distance which corresponds to the equilibrium interatomic distance of the ground state van der Waals molecule. For Xe[5p⁵(²P_{1/2})ns (nd)] + Ar(¹S₀) one obtains 0.06 eV and for Xe(¹S₀) + Kr[4p⁵(²P_{1/2})ns (nd)] 0.10 eV. These values are found to be in agreement with what one would expect from a charge induced-dipole interaction.

B. Manuscripts under preparation:

1. Supersonic Oxygen Atom Beam Source, S. Sibener, and Y. T. Lee, (to be submitted to Rev. of Sci. Instrum.).
2. Crossed Molecular Beams Studies of $O + ICl \rightarrow IO + Cl$, S. Sibener, R. Buss, and Y. T. Lee, (to be submitted to J. Chem. Phys.).
3. Reaction of $O + C_2H_5I$, CF_3I , S. Sibener, R. Buss, and Y. T. Lee, (to be submitted to J. Chem. Phys.).
4. Substitution Reactions of $Cl + 1-, 2-, 3\text{-bromopropene}$, S. Sibener and Y. T. Lee.

DISTRIBUTION LIST

	<u>No. Copies</u>
Office of Naval Research Code 473 Arlington, VA 22217 Attn: Dr. Miller	10
Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106 Attn: Dr. R. Marcus	1
Office of Naval Research Branch Office 536 S. Clark Street Chicago, IL 60605 Attn: Dr. J. Smith	1
Defense Documentation Center Bldg. 5 Cameron Station Alexandria, VA 22314	12
Office of Naval Research Branch Office 495 Summer Street Boston, MA 02210 Attn: Dr. L. H. Peebles	1
Office of Naval Research Resident Representative University of California 553 Evans Hall Berkeley, California 94720	1
U. S. Naval Research Laboratory Code 2627 Washington, DC 20375	6
U. S. Naval Research Laboratory Code 2629 Washington, DC 20375	6

Naval Research Laboratory Code 6100 Washington, DC 20375	1
Naval Air Systems Command Code 440 Washington, DC 20360 Attn: Dr. H. Rosenwasser	1
Naval Sea Systems Command SEA-0331 Washington, DC 20362 Attn: Mr. J. Murrin	1
Naval Sea Systems Command SEA-0332 Washington, DC 20362 Attn: Dr. A. Amster	1
Naval Surface Weapons Center Research and Technology Dept.-WR Silver Spring, MD 20910	1
Naval Weapons Center Research Department Code 60 China Lake, CA 93555	1
Naval Weapons Center Code 608 China Lake, CA 93555 Attn: Ronald L. Derr	3
Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, DC 20332	1
Air Force Office of Scientific Research Directorate of Chemical Sciences Bolling Air Force Base Washington, DC 20332	1
Air Force Office of Scientific Research Directorate of Physics Bolling Air Force Base Washington, DC 20332	1

U.S. Army Research Office
Chemistry Division
P.O. Box 12211
Research Triangle Park, NC 27709

1

U.S. Army Research Office
Physics Division
P.O. Box 12211
Research Triangle Park, NC 27709

1

Professor S.N.B. Murthy
Technical Director, Project SQUID
Purdue University
Lafayette, IN 47907

5

78